

Coal volatiles post pyrolysis in a two staged reactor

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INTRODUCTION

The aim of this paper is to present some new results about volatiles post pyrolysis of the low rank, french, Gardanne coal. Direct pyrolysis of this peculiar coal has been earlier described, with special consideration of light gases release (1)(2) and solid evolution (3)(4). Focusing now on volatiles transformation, we use a two staged reactor where volatiles, produced in the first stage, undergo post pyrolysis in the second stage. After a first study where second stage temperature was kept close to first stage temperature (5), one observation is enlarged here to a wider second stage temperature range.

Compared to other coal tar pyrolysis studies where products are collected at the end of experiments (6)(7)(8)(9), one experimental device is designed as to follow light gases flow rates during post pyrolysis experiments as a function of volatiles production temperature in first stage and of post pyrolysis temperature in second stage.

EXPERIMENTAL

The Gardanne, or Provence, french coal studied here is a low rank one, from Upper Cretaceous, with following characteristics :

Prox. anal. (wt %) - Moisture : 9.6, Ash : 7.4, VM : 45.1

Ult. anal. (wt %, daf) - C : 74.9, H : 5.3, O : 11.3, N : 2.0, S : 5.4

The two staged reactor has been already described (2)(5). It is composed of two stainless steel cylindrical stages series connected and independently heated. Coal sample of 10 g were placed as a thin bed in middle of first stage, supported by carborundum particles deposited on the steel grid present at the bottom of each stage. Carborundum particles also filled second stage as to ensure thermal equilibrium. Coal particles were sized between 0.4 mm and 0.5 mm so that coal bed was formed, on an average, of four particles layers. Carrier gas was N_2 which entered first stage with $33 \text{ cm}^3\text{min}^{-1}$ flowrate. Gaseous effluent was cooled in two successive traps and, after partial condensation, introduced into GC for analysis.

For each experiment, once the reactor was filled and fitted as above described, second stage was heated up to the predetermined T_2 value while N_2 flowed across the whole reactor and first stage remained at ambient temperature. When the predetermined T_2 value was

reached, it was held constant and first stage began to be heated at $3^{\circ}\text{C min}^{-1}$ heating rate : temperature T_1 of first stage was then measured at the same time that gases were introduced in GC.

RESULTS AND DISCUSSION

General features and results presentation

In one stage experiments, it was found that among the nine gases studied, four were largely predominant (CO , CO_2 , H_2 , CH_4) and five appeared as minor gases (C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , H_2S). For the last three gases, flow rate which was already very low in one stage experiments became lower in two stages experiments and rapidly undetectable with increasing T_2 values. In sake of illustrating T_2 influence upon gases flow rate, results are presented as flow rate v.s. T_2 curves for CH_4 , H_2 , CO , CO_2 , C_2H_4 and C_2H_6 (fig. 1 to 6) and as flow rate v.s. T_1 curves for C_3H_6 , C_3H_8 and H_2S (fig. 7 to 9).

When flow rates are plotted against second stage temperature for different T_1 values, post pyrolysis of volatiles, main purpose of these experiments, is only concerned by T_2 values higher than T_1 . However results for T_2 lower than T_1 are also quoted : they show how volatiles cooling in second stage may influence gases flow rates, keeping in mind that this cooling always maintain volatiles above 600°C .

Increasing first stage temperature, T_1 became equal to T_2 and situation occurred where volatiles were kept in second stage at their production temperature in first stage. Compared to one stage experiments, two stages experiments lead thus to increase residence time of volatiles at their production temperature, giving indication upon residence time influence on gases flow rate.

Although main purpose of this study was volatiles post pyrolysis on an, as possible, inert solid, when second stage temperature exceeded 700°C , coke was found in second stage, deposited on carborundum particles and internal reactor walls. In conditions described in experimental part, and taking into account that apparatus was not conveniently suitable for quantitative solid recuperation, coke traces are observed at 800°C and averaged weights of 40 mg and 500 mg respectively measured at 900°C and 1000°C .

Carbon dioxide

Before coke deposition, T_2 rise has a positive effect on CO_2 flow rate (fig. 1). With coke present in second stage, at T_2 higher than 800°C , two different effects are observed according to first stage temperature range : the effect of T_2 rise is positive for low values of T_1 (500 to 600°C) and negative for higher T_1 values. Cooling volatiles from 700°C and 800°C to lower temperatures decreases CO_2 flow rate.

Volatiles are assumed to contain CO_2 precursors which require for decomposition temperatures higher than their production temperature in first stage. Decomposition into CO_2 is also enhanced by longer residence time, as we observed positive effect of residence time upon CO_2 flow rate at 700°C and 800°C . These decomposition reactions appear to be reversed when cooling volatiles from 700°C and 800°C to lower temperature. Above 800°C , T_2 value, CO_2 flow rate increase is related to reaction with deposited coke, this reaction being less complete when volatile are produced at low T_1 (500°C to 600°C).

Carbon monoxide

In absence of coke, CO flow rate is little changed by post pyrolysis temperature rise. Compared to one stage experiments, two stages experiments lead to CO flow rate decrease of about 25 % for 600 to 800 common values of T_1 and T_2 . Inversely cooling volatiles from 600°C to 700°C increases CO flow rate (fig. 2). In presence of coke, CO flow rate increases with T_2 rise, for all T_1 values and this increase is more important the lower the volatiles production temperature T_1 .

These results do not allow definitive conclusions about predominance of CO production or consumption reactions involatiles below 800°C : we may only conclude to existence of such reactions from decrease of CO flow rate for higher residence time and from CO increase when cooling volatiles. At higher temperature of second stage, when coke is deposited, CO flow rate increase is partly ascribed to reaction of CO_2 with coke, what explains also CO_2 flow rate decreases observed on figure 1. Other part of CO production increase is assumed to reaction between coke and water produced in primary pyrolysis and present in volatiles released below 600°C .

Hydrogen

Variations of H_2 flow rate with second stage temperature seem qualitatively like CO ones, with H_2 flow rate about twice CO one (fig. 3). Below 800°C , effect of T_2 rise is weakly positive, effect of residence time is negative except for 800°C where it becomes unappreciable and cooling volatiles decreases H_2 flow rate. Above 800°C , T_2 has positive effect upon H_2 flow rate and this effect is more important when volatiles are produced below 600°C than when produced above 600°C .

In absence of coke, H_2 flow rate variations result from competition between H_2 producing and H_2 consuming reactions which may be mainly hydrocarbons cracking, deshydrogenation and aromatisation of H_2 production and hydrocracking for H_2 consumption. From our observations, in this competition H_2 producing reactions would be favoured by higher post pyrolysis temperature while H_2 consuming ones would be promoted by longer residence time and lower temperature. In presence of coke (at the end of experiment), as for CO, H_2 flow rate increase may be partly ascribed to water reaction with coke, forming simultaneously CO and

H₂, when volatiles are produced below 600°C and contain thus quantity of water. For T₁ value above 600°C, volatiles do not contain more water and H₂ production is only related to aromatisation and cokefaction.

Methane

CH₄ flow rates are in the range of H₂ ones, but evolution with T₂ is quite different (fig. 4). Up to 650°C T₁ value, CH₄ flow rate show two maxima, for T₂ values of 700°C and 850°C, and a minimum between 750°C and 950°C. For T₁ higher than 650°C, CH₄ flow rate decreases when T₂ varies from 800°C to 1000°C. Cooling volatiles from 700°C and 800°C to lower temperature in second stage decreases CH₄ flow rate and residence time has positive effect upon this flow rate, of 60 % at 700°C and 480 % at 800°C.

CH₄ production in second stage is ascribed to cracking and hydrocracking reactions below 800°C T₂ value and to cokefaction above 800°C. Parallel to cracking and hydrocracking reactions, aromatisation occurs when T₂ rises above 700°C, decreasing thus CH₄ flow rate after the maximum shown at 700°C. Above 800°C, cokefaction occurs and releases CH₄, what increases CH₄ flow rate till maximum at 950°C, above which temperature cokefaction does not release more CH₄. CH₄ precursors chemical groups appear to be different for cracking reactions and cokefaction, as first maximum related to cracking reactions increases for higher T₁ values and second maximum, related to cokefaction, decreases for higher T₁ values.

C₂ hydrocarbons

C₂H₄ flow rate evolution looks like CH₄ one when T₂ increases with two maxima, at 700°C and 950°C, for T₁ lower than 700°C and with a rapid decrease for T₁ higher than 700°C (fig. 5). Maximum at 700°C is assumed to result from competition between cracking and deshydrogenation reactions, predominant below 700°C, and aromatisation reactions which prevail above 700°C.

C₂H₆ evolution is different from C₂H₄ one, specially by shifting of maximum flow rate to higher T₂ values when T₁ increases (fig. 6). Assuming that C₂H₆ decomposition reaction is the same, very probably deshydrogenation, for all T₁ values, maximum shifting is ascribed to difference in chemical nature of C₂H₆ precursors when volatiles production temperature varies.

C₃ hydrocarbons and hydrogen sulfide

C₃ hydrocarbons and hydrogen sulfide rapidly disappear from volatiles when second stage temperature increases (fig. 7, 8, 9). For C₃ hydrocarbons, it is evident that disappearance is related to numerous consumption reactions like cracking, deshydrogenation and aromatisation. H₂S is known to decompose in the temperature range of second stage operating.

CONCLUSION

The above experiments of coal volatiles post pyrolysis in a two staged reactor give informations upon respective influence of pyrolysis and post pyrolysis temperatures on light gases production. Such two stages experiments allow to relate light gases production to volatiles composition and to distinguish between temperature ranges where solid coke is, or not, deposited. Results confirm influence of residence time upon post pyrolysis reactions and go further in details of peculiar effects. Slow cooling of volatiles, in temperature range where they remain reactive, modify gaseous flow rates, indicating thus volatiles evolution between reacting place and analysis inlet.

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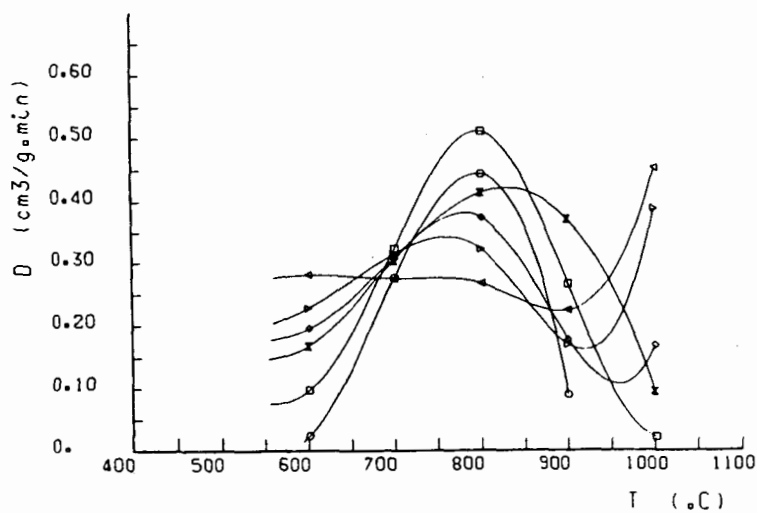


FIG 1 CO₂ FLOW RATE VS SECOND STAGE TEMPERATURE
FIRST STAGE TEMPERATURE:
△ 500°C, ▽ 550°C, ○ 600°C, × 650°C, □ 700°C, ○ 800°C

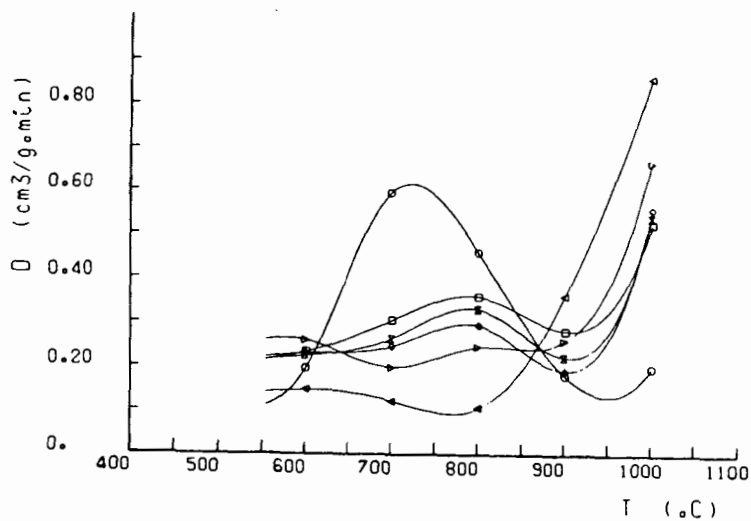


FIG 2 CO FLOW RATE VS SECOND STAGE TEMPERATURE
FIRST STAGE TEMPERATURE:
△ 500°C, ▽ 550°C, ○ 600°C, × 650°C, □ 700°C, ○ 800°C

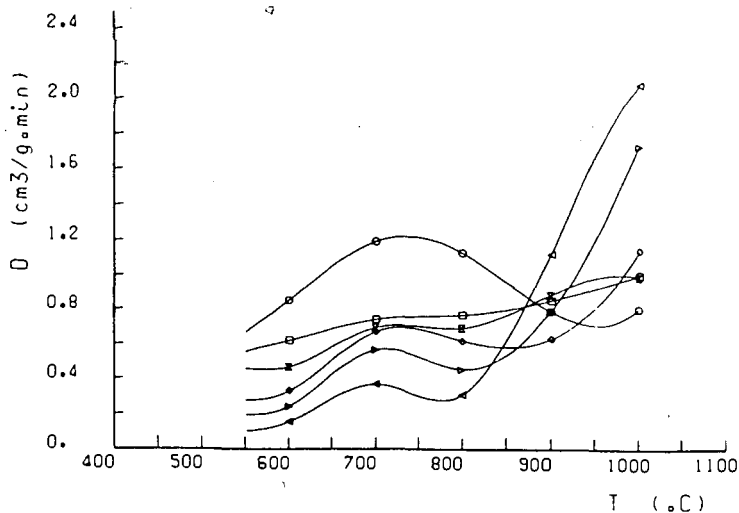


FIG 3 H₂ FLOW RATE VS SECOND STAGE TEMPERATURE
FIRST STAGE TEMPERATURE:
▲ 500°C, ▴ 550°C, ○ 600°C, × 650°C, □ 700°C, ○ 800°C

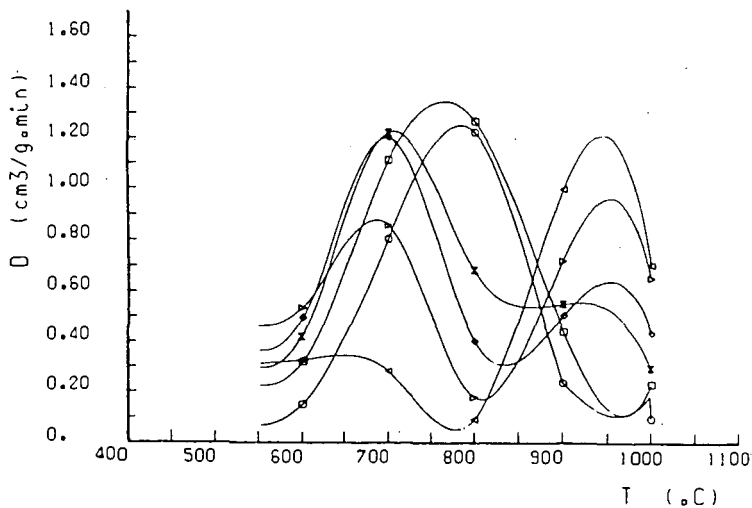


FIG 4 CH₄ FLOW RATE VS SECOND STAGE TEMPERATURE
FIRST STAGE TEMPERATURE:
▲ 500°C, ▴ 550°C, ○ 600°C, × 650°C, □ 700°C, ○ 800°C

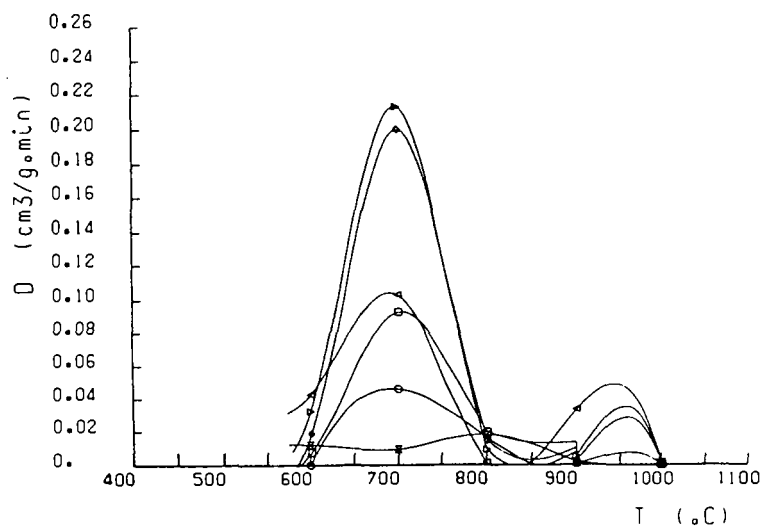


FIG 5 C₂H₄ FLOW RATE VS SECOND STAGE TEMPERATURE
FIRST STAGE TEMPERATURE :
△ 500°C. ▾ 550°C. ○ 600°C. ⋈ 650°C. □ 700°C. ○ 800°C

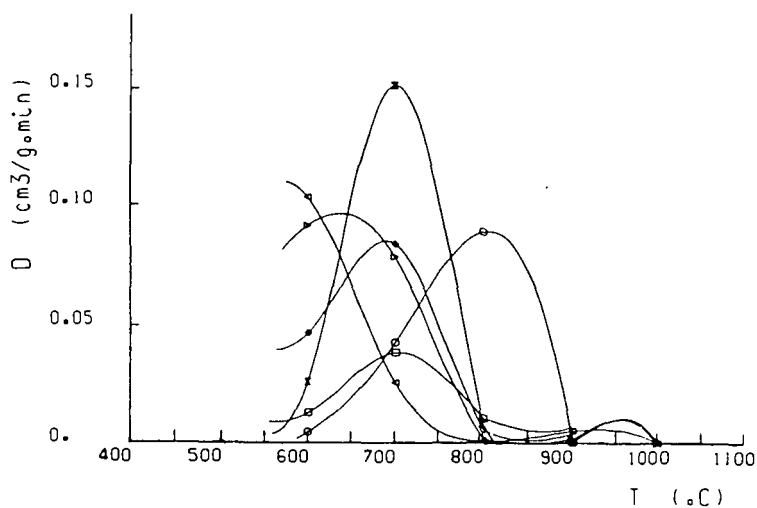


FIG 6 C₂H₄ FLOW RATE VS SECOND STAGE TEMPERATURE
FIRST STAGE TEMPERATURE :
△ 500°C. ▾ 550°C. ○ 600°C. ⋈ 650°C. □ 700°C. ○ 800°C

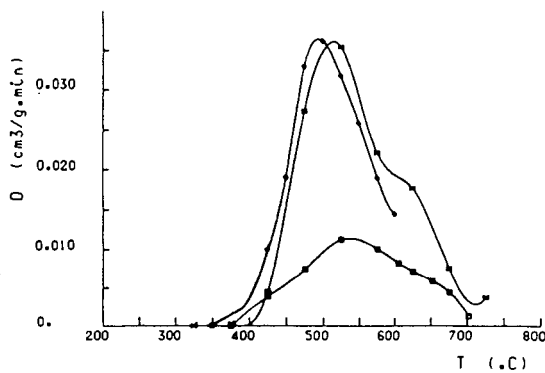


FIG 7 C₃H₆ FLOW RATE VS FIRST STAGE TEMPERATURE
SECOND STAGE TEMPERATURE
○ 600°C, □ 700°C, ONE STAGE 2nd

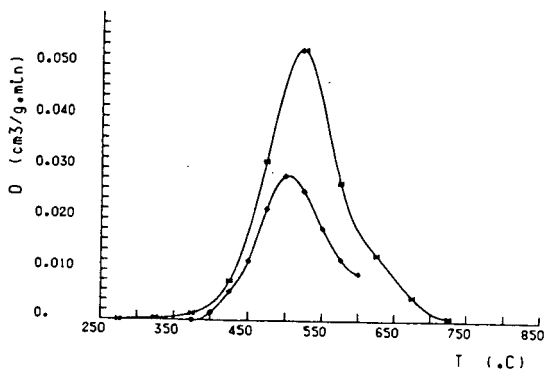


FIG 8 C₃H₆ FLOW RATE VS FIRST STAGE TEMPERATURE
SECOND STAGE TEMPERATURE
○ 600°C, □ 700°C, ONE STAGE 2nd

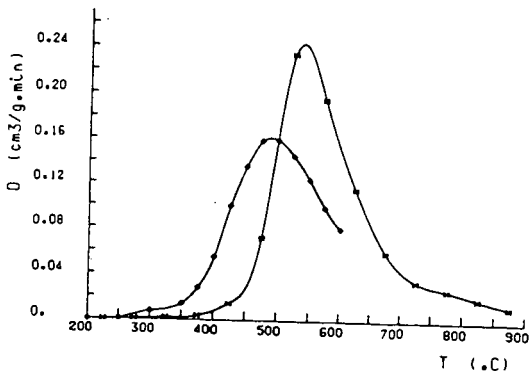


FIG 9 H₂ FLOW RATE VS FIRST STAGE TEMPERATURE
SECOND STAGE TEMPERATURE
○ 600°C, □ 700°C, ONE STAGE 2nd